Infrared Spectroscopic and Electronic Structure Investigations of Beryllium Halide Molecules, Cations, and Anions in Noble Gas Matrices

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Supporting Information

ABSTRACT: Laser-ablated Be atoms, cations, and electrons were reacted with F_2 , ClF, Cl₂, NF₃, CCl₄, CF₂Cl₂, HCl, DCl, and SiCl₄ diluted in noble gases. The major products were the dihalides BeF₂, BeClF, BeCl₂, and the hydride chloride HBeCl, whose identities were confirmed by comparison with previous evaporative work, deuterium substitution, and vibrational frequency calculations. The matrix-isolated fundamental frequency of the BeF molecule is higher, and the frequency of BeCl⁺ cations formed strong dipole-induced dipole complexes in solid Ne, Ar, Kr, and Xe with stepwise increase in computed noble gas dissociation energies. Going down the family NgBeF⁺ and NgBeCl⁺ series (Ng = Ne, Ar, Kr, Xe) the Mulliken charges q(Be)



decrease, while q(Ng) increases, and the dipole moments decrease, which suggests covalent bonding in the xenon species. We find that the largest intramatrix shift is Ne to Ar which follows the largest factor increase for the Ng atomic polarizabilities. Extra electrons produce Cl⁻, which reacts with HCl to form the stable HCl₂⁻ anion and possibly with BeCl₂ to give BeCl₃⁻. A weak band observed in neon experiments with F₂ is probably due to BeF₃⁻.

INTRODUCTION

One of our earliest laser ablation targets for matrix infrared investigations was boron, which upon condensation with oxygen/argon samples, provided a number of new boron oxides.¹ Boron is difficult to evaporate because of container problems with the liquid, but this is avoided by focused pulsed laser ablation of a small amount of material, mostly atoms, from a solid target. Since Be forms toxic compounds such a method, which presents a trace amount of atoms for reaction, is desired. Accordingly we have reacted laser ablated Be atoms with small molecules such as O₂, CO₂, H₂, CO, HCN, and C₂H₂.²⁻⁸ Of most interest here is our discovery of the Ar-BeO complex^{2,3} and the simplest triatomic molecule BeH2.5 The most interesting property of BeO in an argon matrix is that the observed frequency, 1526.1 cm⁻¹, is higher than the gas-phase diatomic molecule frequency⁹ by 62.4 cm⁻¹, and the oxygen 16/18 frequency ratio 1.0190 is slightly lower than the calculated anharmonic ratio 1.0207 for the diatomic BeO molecule.² Ionic diatomic molecules typically exhibit large red shifts when trapped in an argon matrix, for example, the major absorption for the isoelectronic molecule LiF in solid argon is at 838 cm⁻¹, which is 56.5 cm⁻¹ lower than the gas-phase fundamental frequency (894.5 cm⁻¹).^{9,10} From this comparison Thompson and Andrews concluded that Ar-BeO forms a bound dipole-induced dipole complex: additional experiments using Kr and Xe formed even stronger complexes with BeO.^{2,3}

Veldkamp and Frenking computed these noble gas complexes to be bound by 6.7, 9.3, and 12.6 kcal/mol, respectively.¹¹

Following this special behavior for beryllium with an electronegative partner, we decided to investigate beryllium halides. The \mbox{BeF}_2 and \mbox{BeCl}_2 molecules have been observed in noble gas matrices¹² and in the gas phase,¹³ and the frequencies of the monohalides are known from gas-phase electronic spectra.⁹ We find that BeF₂ has antisymmetric stretching frequencies in solid neon and argon that are 26 and 9 cm⁻ above the gas-phase value (1520 cm^{-1}) and that the BeF diatomic molecule fundamental in solid Ne, Ar, and Kr is 13.0, 5.6, and 0.5 cm^{-1} higher than the gas-phase mode (1229.2 cm⁻¹).⁹ The chlorine counterparts exhibit similar behavior: the $BeCl_2$ absorption is 12 cm⁻¹ above (in neon) and 1 cm⁻¹ below (in argon) the gas-phase measurement (1113 cm^{-1}), and BeCl is 4.2, 19.0, and 25.0 cm⁻¹ below (in Ar, Kr, Xe) the gas-phase mode (837.0 cm^{-1}). These comparisons show that the matrixisolated Nen-BeF, Arn-BeF, and Krn-BeF dipole-induced dipole complexes are stronger than the chlorine counterparts, and the possibility of cation complexes must also be considered.

Pulsed laser ablation is known to produce metal cations from mass spectroscopy and ion cyclotron resonance investiga-

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tions.^{14,15} Accordingly, an extensive array of transition-metal carbonyl cations, neutrals, and anions has been observed in argon and neon matrixes based on ¹³C and ¹⁸O substitution in the infrared spectra, the effect of adding the electron-trapping CCl₄ molecule to increase the infrared intensity of cation absorptions and decrease the intensity of anion products, and agreement with density functional frequency calculations.^{16–19} In addition the laser ablation plume contains high-energy UV radiation, which can photoionize the metal atoms during the matrix condensation process.²⁰ In the following paper we report the BeF⁺ and BeCl⁺ cations in matrices and find that the calculated values for the Be-X stretching modes of Ne-BeF⁺ and Ne-BeCl⁺ are 15 and 61 cm⁻¹ higher than the computed values for the isolated diatomic cations, and the calculated dissociation values for Ne from these complexes are 12 and 11 kcal/mol. We are not aware of gas-phase optical spectra of these cations. The new molecules HBeCl and FBeCl were also identified by matrix infrared spectra and theoretical frequency calculations.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Laser-ablated beryllium atoms and cations produced by Nd:YAG laser (Continuum Minilite II) evaporation from the solid (Johnson-Matthey, lump, 99.5%) were codeposited with dilute mixtures (0.1-3.0%) of reagent gas (F₂, ClF, Cl₂, NF₃, CF₂Cl₂, CCl₄, and SiCl₄ from Air Products and Chemicals, Ozark-Mahoning, Matheson, Air Products and Chemicals, Yonghe Refrigerant, Sinopharm Chemical Reagent, Alfa Aesar, respectively) in neon, argon, krypton or xenon (Spectra Gases). The fluorine-bearing manifold was thoroughly passivated with F₂ before use, and this manifold was treated with 150 torr of ClF overnight before use. Matrix/reagent samples were codeposited onto a CsI window cooled to 4 K using a closed-cycle refrigerator (Sumitomo): the window was heated to 17 ± 1 K for krypton at Virginia. These methods have been described in detail elsewhere.^{7,16,20,21} After deposition, infrared spectra were recorded at a resolution of 0.5 cm⁻¹ and accuracy of 0.1 cm⁻¹ using a Nicolet iS50 spectrometer (in Virginia) with MCT-A (4000 to 640 cm⁻¹) and DTGS-KBr (4000 to 540 cm⁻¹) detectors or a Bruker Vertex 80v (in Shanghai) with an MCT-B (4000 to 440 cm^{-1}) detector. Matrix samples were warmed and recooled (annealed, gold/ cobalt vs chromel thermocouple temperature measurement), and more spectra were recorded. The samples were irradiated by a mercury arc street lamp (Sylvania, 175 W, outer globe removed, $\lambda > 220$ nm) for 10 min periods, and more spectra were recorded. Additional annealings were performed, and final spectra were recorded.

Theoretical calculations for possible reaction products were performed with the Gaussian 09 package.²² In all instances, the B3LYP hybrid density functional^{23,24} was used, and Be, F, Cl, Ne, Ar, Kr, and hydrogen atoms employed the large 6-311+ +G(3df,3pd) Gaussian basis²⁵ and cc-pVTZ basis,²⁶ but the heavier Xe atom required the SDD²⁷ or cc-pVTZ-PP²⁶ pseudopotential and basis set. Such density functional theory (DFT) calculations predict vibrational frequencies with reasonable accuracy for metal compounds.^{4,7,16,20,28,29} Geometries were fully relaxed during optimization, and the optimized geometries were confirmed by vibrational analysis. Separate calculations with CCSD(T)³⁰ were employed to supplement the B3LYP results. The zero-point energy is included in the calculation of binding energy for a metal complex, and it is corrected for the basis set superposition error (BSSE) using the full counterpoise method of Boys and Bernardi.³¹ Localized orbital locator (LOL) and the non-covalent interaction index (NCI)³² was introduced to investigate the matrix interaction performed with the Multiwfn program³³ and visualized using the VMD package.³⁴

RESULTS AND DISCUSSION

Laser-ablated beryllium atoms, cations, and electrons were codeposited with F_2 , NF_3 , CIF, Cl_2 , CF_2Cl_2 , CCl_4 , and $SiCl_4$ diluted in noble gases, and the observations were compared with previous work and density functional calculations of energies, structures, and harmonic vibrational frequencies.

Infrared Spectra of Beryllium Fluorides. Figure 1 illustrates the neon matrix spectra of 1% F₂ reacted with



Figure 1. Infrared spectra in the product absorption regions for laserablated Be atoms and cations codeposited with F_2 in excess neon at 4 K: (a) Be + 1.0% F_2 in Ne codeposited for 50 min. (b) After photolysis with $\lambda > 220$ nm for 10 min, (c) after annealing to 8 K, and (d) after annealing to 10 K.

laser-ablated beryllium atoms, which is dominated by a very strong 1546.5 cm⁻¹ absorption for BeF₂ that is in agreement with Snelson's neon matrix measurement of a strong band labeled 1545 in the published spectrum using a prism instrument, but 1542 cm⁻¹ was listed in the table of frequencies.¹² That early work codeposited thermally evaporated molecules from the solid at high temperature (600-1000 °C) with neon onto a window at 4 K and made frequency measurements with a prism spectrometer, which is not as accurate as current Fourier transform IR instruments. Figure 1 also shows common fluorine impurity bands for CF₄ at 1277.7 and OCF_2 at 1237.5 cm⁻¹ and the growth of absorption at 1490-1500 cm⁻¹ on annealing, which arises from the OOF radical owing to O₂ impurity in the fluorine sample.³⁵ A weak new band labeled BeF was observed at 1241.6 cm⁻¹ with a slightly higher frequency shoulder: this feature is higher than the gas-phase 1229.2 cm⁻¹ frequency for BeF.⁹ Product absorptions are listed in Table 1. Irradiation of the sample with the full light of the mercury arc ($\lambda > 220$ nm) for 10 min increased the BeF₂ feature by 40%, while BeF decreased by ~10%. Annealing the sample to 8 K almost doubled the latter band and decreased the former band by $\sim 20\%$: the final annealing to 10 K slightly decreased both features. Annealing also increased a weak band at 1252 cm⁻¹ in Figure 1d, which can be assigned to $(BeF_2)_2$ based on additional work of Snelson.³⁶ Two additional neon matrix experiments gave similar product absorptions.

Nitrogen trifluoride is also a good fluorine atom source, and Figure 2 shows the reaction of Be with a 0.5% sample in neon. The first spectrum is a predeposition of 5% of our sample

Table 1. Infrared Absorptions for Beryllium Halide Molecules from Reactions with Halogen Molecules in Noble Gas Matrixes

molecules	neon	argon	krypton
BeF ₂	1546.5	1529.4	1525.8, 1541.6
BeF	1242.2, 1241.6	1234.8	1229.7
BeF ⁺	1457.8	1445.0	1449.1, 1445.0
Be ³⁵ Cl ₂	1125.2	1111.6	1102.7
Be ^{35,37} Cl ₂	1123.5	1109.9	1101.1
Be ³⁷ Cl ₂	1121.8	1108.2	1099.3
BeCl		818.8	
$BeCl^+$	1001.4	996.4, 994.8	989.8
BeClF	1391.9	1375.6	1371.3
BeF ₃ ⁻	1061.4 (tentative)		



Figure 2. Infrared spectra in the product absorption regions for laserablated Be atoms and cations codeposited with NF₃ in excess neon at 4 K: (a) predeposition of 0.5% NF₃ in Ne for 10 min, (b) same sample codeposited with Be for 50 min, (c) after annealing to 8 K, and (d) after photolysis with $\lambda > 220$ nm for 10 min.

without Be: in this region two NF₃ bands were observed at 1540.4 and 1519.3 cm⁻¹, and CF₄ and OCF₂ were again observed. The BeF₂ band at 1546.5 cm⁻¹ was approximately the same intensity (0.06 absorbance units) as in the reaction with F₂, and the BeF feature appeared at 1242.2 cm⁻¹ with a lower-frequency shoulder. The NF and NF₂ photolysis products were observed at 1119.8 and 936.1 cm⁻¹, which shows that F atoms are produced for reaction partners.^{9,35} Full arc photolysis increased the BeF₂ band by 30% and almost destroyed the BeF peak.

The corresponding spectrum with Be and F_2 (2%) in argon is illustrated in Figure 3. Codeposition for 50 min with Be produced a strong sharp new band at 1529.4 cm⁻¹, a weaker band at 1445.0 cm⁻¹, and a new feature at 1234.8 cm⁻¹ below the OCF₂ peak. Notice that the OOF radical is observed at 1489.8 cm⁻¹ from the reaction of F atoms with O₂ impurity in the fluorine,³⁵ and this absorption increased on annealing, decreased on photolysis, and provided more evidence for F atom reactions in the matrix. Sample annealing to 20 K increased the two higher bands and slightly decreased the lower product band. Sample irradiation doubled the two upper bands, decreased the lower band, produced a weaker satellite at 1233.8 cm^{-1} , and increased another band labeled Be_2F_4 at 1246.3 cm^{-1} threefold. Sample annealing to 25 K decreased the strong BeF₂ band, increased the 1445.0 cm⁻¹ feature, and markedly decreased the BeF band. Final annealing to 30 K decreased all of the product absorptions. The highest band at 1529.4 cm^{-1} is close to the 1528 cm⁻¹ assignment of Snelson to BeF₂ in



Figure 3. Infrared spectra in the product absorption regions for laserablated Be atoms and cations codeposited with F_2 in excess argon at 4 K: (a) Be + 2.0% F_2 in Ar codeposited for 50 min. (b) After and annealing to 20 K, (c) after photolysis with $\lambda > 220$ nm for 10 min, (d) after and annealing to 25 K, and (e) after annealing to 30 K.

solid argon, and the weak band at 1246.3 cm⁻¹, which also increased on photolysis, is in agreement with that reported for $(BeF_2)_2$.^{12,36} Another argon matrix experiment reproduced these argon matrix observations.

The following experiment was done with Be and 1% F_2 and 1% Kr in excess argon: the 1529.4 and 1489.2 cm⁻¹ bands were not shifted, but the other two product bands were red-shifted slightly to 1444.7 and 1234.1 cm⁻¹, which suggests a more intimate involvement with the noble gas environment for the latter two absorbing species labeled BeF⁺ and BeF.

The corresponding spectrum with Be and NF₃ (1%) in argon (not shown) produced the same bands as did the F₂ reaction with relatively more of the lower BeF band than the higher BeF₂ band, which was observed more clearly with only a trace of the OCF₂ absorptions. The upper band increased, and the latter band decreased on photolysis as before. The 1445.0 cm⁻¹ band was weaker than with the F₂ reagent, but it behaved the same on photolysis and annealing.

Beryllium atoms were also reacted with 2% F₂ in a krypton matrix deposited at 17 ± 1 K, and the spectra are shown in Figure 4: it is anticipated that a significant proportion of our fluorine will react with krypton under UV light from the



Figure 4. Infrared spectra in the product absorption regions for laserablated Be atoms and cations codeposited with F₂ in excess krypton at 17 ± 1 K: (a) Be + 2.0% F₂ in Ar codeposited for 50 min. (b) After photolysis with $\lambda > 220$ nm for 10 min both recorded using the DTGS-KBr detector, (c) spectrum scanned again using the MCT-A detector. (d) MCT-A spectrum after annealing to 30 K, (e) same after annealing to 40 K.

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ablation plume.^{20,37} The first two spectra were recorded using the DTGS-KBr detector, which enabled scans to lower frequency with much less sensitivity. The first scan for deposition shows a weak 578.4 cm⁻¹ band³⁷ for KrF₂ along with OOF (1487.9 cm⁻¹), CF₄ (1271.6 cm⁻¹), and OCF₂ (1235.0 cm^{-1}) impurities.³⁵ New product bands for BeF₂ were observed at 1525.8 and 1541.6 cm⁻¹, which may be compared with Snelson's bands at 1524 and 1540 cm^{-1.12} In addition a weak feature was observed at 1229.7 cm⁻¹ labeled BeF just below the OCF₂ absorption. Photolysis with the full light of the mercury arc doubled the BeF₂ bands and substantially reduced the BeF band as before, and it increased the KrF₂ absorption by an order of magnitude (Figure 4b). The higher region was scanned again using the more sensitive MCT-A detector (Figure 4c), and virtually the same spectrum was observed along with a weak sharp band at 1449.1 cm⁻¹. Annealing cycles to 30 and 40 K decreased the product absorptions.

Infrared Spectra of Beryllium Chloride Fluoride. Reactions were done with ClF to synthesize BeClF and to explore the reaction mechanism. Figure 5 compares reactions



Figure 5. Infrared spectra in the product absorption regions for laserablated Be atoms and cations codeposited with CIF and Cl₂ + F₂ in excess argon at 4 K: (a) Be + 2.0% CIF in Ar codeposited for 50 min, (b) after annealing to 25 K, (c) after photolysis with $\lambda > 220$ nm for 10 min, (d) Be + 1% F₂ + 1% Cl₂ in Ar codeposited for 50 min, (e) after annealing to 25 K, and (f) after photolysis with $\lambda > 220$ nm for 10 min.

with ClF 2% in argon (a,b,c) and with 1% F_2 and 1% Cl_2 in argon (d,e,f). The strong Cl isotopic doublet observed for ClF at 767.7, 760.5 cm⁻¹ is not shown. The first thing to notice is the sharp new band labeled BeClF at 1375.6 cm⁻¹, which increases slightly on annealing to 25 K without much change in the 1529.4 cm⁻¹ band of BeF₂ and the 1111.6, 1109.9 cm⁻¹ doublet labeled BeCl₂. Full arc photolysis increased the BeFCl band by 50% and the other two dihalides by 20%. In contrast the reaction with F_2/Cl_2 produced less BeFCl and more BeF₂ and BeCl₂, and the latter two species almost double on photolysis, while the former increases only 60%. The BeF band is again observed at 1234.8 cm⁻¹, and it decreased on annealing and photolysis as before.

With neon the ClF molecule has a resolved ³⁵ClF and ³⁷ClF isotopic doublet at 771.6, 764.3 cm⁻¹. Spectra for the reactions of Be and ClF in a neon matrix are provided in Figure S1. In neon the BeF₂ band at 1546.5 cm⁻¹ is the strongest product followed by BeFCl at 1391.9 cm⁻¹ and BeCl₂ at 1125.2, 1123.6 cm⁻¹. It is typical for neon matrix frequencies to be higher and closer to gas-phase frequencies than argon matrix frequencies as described in a noteworthy paper by Jacox.³⁸ The gas-phase fundamental for ³⁵ClF is 773.83 cm⁻¹.

For the reaction with ClF in krypton BeClF is the strongest product band at 1371.3 cm⁻¹ followed by BeCl₂ at 1102.3 cm^{-1} : BeF₂ was apparently not formed in Kr by diffusing F atoms, reactions 3 and 4 in sequence, due to the favored reaction to make KrF₂. However, bimolecular reaction 1 with Be and F_2 to form BeF₂ can compete with the Kr + F_2 reaction (Figure 4). Therefore, the primary reaction is Be insertion into the halogen molecule to make the dihalide product molecules, which are relaxed and trapped in the matrices. These are all exothermic reactions 1, and they can proceed on sample deposition and on UV photolysis. Some of the [BeX₂]* decomposes to BeX + X, reaction 2. The energy changes for reactions 1, 2, 3, and 4 with F₂ are negative 272, 106, 140, and 166 kcal/mol using B3LYP/6-311++G(3df,3pd). Laser-ablation plume photolysis can, of course, photodissociate the halogen molecules, and the Be addition reactions 3 and 4 can occur particularly during the annealing process with solid neon and argon. The energies for reaction 1 using the ClF and Cl₂ reagents are negative 206 and 168 kcal/mol. Both CCl4 and SiCl₄ serve as Cl atom sources for laser-ablated Be by direct reactions 5 and 5') and through laser-plume photolysis.

$$Be + X_2 \to [BeX_2]^* \to BeX_2 \tag{1}$$

$$Be + X_2 \rightarrow [BeX_2]^* \rightarrow BeX + X \tag{2}$$

$$Be + X \rightarrow [BeX]^* \rightarrow BeX$$
 (3)

$$BeX + X \to [BeX_2]^* \to BeX_2 \tag{4}$$

$$Be + CCl_4 \rightarrow [BeCCl_4]^* \leftrightarrow BeCl + CCl_3 \tag{5}$$

$$Be + SiCl_4 \rightarrow [BeSiCl_4]^* \rightarrow BeCl + SiCl_3$$
(5')

We also observe from the argon CIF experiment (Figure 5) that BeCIF increases the most on UV photolysis, reaction 1', and that BeF₂ is much more intense than BeCl₂, which suggests that reaction 2' favors the more exothermic formation of BeF over BeCI. The computed energies for reaction 2' and 2" are negative 81 and 36 kcal/mol, respectively (B3LYP/6-311++G(3df,3pd)). In addition F atoms from photodissociation of CIF by the laser-ablation plume²⁰ will diffuse more readily through the argon matrix on annealing than will Cl atoms, so reactions 3' and 4' are more likely to proceed with F than with Cl atoms.

 $Be + ClF \rightarrow [BeClF]^* \rightarrow BeClF \tag{1'}$

$$Be + ClF \rightarrow [BeClF]^* \rightarrow BeF + Cl$$
(2')

$$Be + ClF \rightarrow [BeClF]^* \rightarrow BeCl + F$$
(2")

$$Be + F \to [BeF]^* \to BeF \tag{3'}$$

$$BeF + F \to [BeF_2]^* \to BeF_2 \tag{4'}$$

Reactions were also done with CCl_2F_2 in an argon matrix (Figure S2), and BeClF, BeF₂, BeF, BeCl₂, and BeCl were observed. Notice such reactions gave less BeF₂ and BeF than BeCl₂ and BeCl, since the C–F bond from CCl_2F_2 is harder to cleave than the C–Cl bond during laser ablation.

Infrared Spectra of Beryllium Chlorides. Experiments were performed for Be and Cl_2 in the Ne, Ar, and Kr matrices, and the major product band in each case was a resolved chlorine isotopic triplet, which is shown in Figure 6 for all three, and the peaks are listed in Table 1. A weak higher-frequency peak in the neon and argon matrixes is probably due



Figure 6. Infrared spectra in the Be–Cl stretching region for laserablated Be atoms and cations codeposited with Cl₂ in excess neon, argon, and krypton: (a) Be + 1.0% Cl₂ in Ne codeposited for 50 min at 4 K. (b) After photolysis with $\lambda > 220$ nm for 10 min, (c) after annealing to 10 K; (d) Be + 2.0% Cl₂ in Ar codeposited for 50 min at 4 K. (e) After photolysis with $\lambda > 220$ nm for 10 min, (f) after annealing to 25 K; (g) Be + 3.0% Cl₂ in Kr codeposited for 50 min at 17 K. (h) After annealing to 35 K, (i) after photolysis with $\lambda > 220$ nm for 10 min.

to a matrix site splitting. The broad band at 1116 cm^{-1} in the neon sample is probably due to BeCl₂ complexed with Cl₂ reagent, as isolation is more difficult to achieve in the lower-freezing neon matrix. A weak 818.8 cm⁻¹ band is observed to track with the strong isotopic triplet for BeCl₂ in argon, and it is assigned to BeCl based on agreement with the following work

involving Be atom reactions with the chlorine-bearing reagents CCl_4 and $SiCl_4$.

Figure 7 compares spectra for Be atom reactions with CCl_4 and $SiCl_4$ in excess neon as sources for Cl atoms, and the major product frequencies are listed in Table 2. Notice the bands

Table 2. Observed Vibrational Frequencies (cm^{-1}) of Major CCl_4 and $SiCl_4$ Reaction Products in Matrixes

molecules	neon	argon	krypton	xenon
BeCl ₂	1125.3	1111.5	1102.5	1096.1
	1123.6	1109.8	1101.1	
	1121.9	1108.3	1099.1	
BeCl	832.8	817.7	812.0	811.5
	828.2	813.4	807.4	806.3
HBeCl		2117.6	2111.4	2108.5
	811.8	800.4	795.0	790.7
	806.8	795.6	790.2	785.9
		515.6	508.7	500.2
DBeCl		1613.1	1607.1	
	775.7	768.6	764.2	760.5
	770.8	763.7	759.5	755.7
BeCl ⁺	1001.7	995.9		
	998.3	993.0		
$BeCl_3^-$ (tentative)	710.8	705.6	688.9	686.5
				678.8
HCl_2^-	738	696	663	644

common to both experiments: the strongest such product absorption is the triplet of bands starting at 1125.3 cm⁻¹ and labeled BeCl₂, which are within 0.1 cm⁻¹ of the triplet components observed from the Be reaction with chlorine in Figure 6. Next a doublet of bands is observed at 832.8 and 828.2 cm⁻¹, which is labeled BeCl. This band is very close to



Figure 7. Infrared spectra in the product absorption regions for laser-ablated Be atoms and cations codeposited with SiCl₄ or CCl₄ in excess neon at 4 K: (a) Be + 0.1% SiCl₄ in Ne codeposited for 50 min, (b) after annealing to 10 K, (c) after photolysis with $\lambda > 220$ nm for 10 min, (d) after annealing to 12 K; (e) Be + 0.1% CCl₄ in Ne codeposited for 50 min, (f) after annealing to 10 K, (g) after photolysis with $\lambda > 220$ nm for 10 min, (h) after annealing to 12 K.

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Table 3. Calculated Vibrational Frequencies	(cm^{-1}) and	l Intensities (km	n/mol, in Parent	theses) of Major Products
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	B3L	LYP/6-311++g(3df,3	Bpd)			CCSD(T)/cc-pVTZ			
	35-Cl	35,37-Cl	37-Cl	35-Cl	35,37-Cl	37-Cl	35-Cl	35,37-Cl	37-Cl
BeCl ₂	1133.2(438)	1131.4(437)	1129.7(436)	1133.3(424)	1131.5(422)	1129.8(421)	1144.5	1142.7	1140.9
	400.4(0)	395.0(0)	389.5(0)	399.4(0)	394.0(0)	388.5(0)	402.1	396.6	391.1
	$246.7(45 \times 2)$	$246.3(45 \times 2)$	$245.9(45 \times 2)$	$241.3(45 \times 2)$	$240.9(45 \times 2)$	$240.5(45 \times 2)$	235.2	234.9	234.5
BeCl	835.7(126)		831.1(125)	832.3(122)		827.7(121)	841.6		836.9
HBeCl	2210.6(162)		2210.6(162)	2204.7(161)		2204.7(161)	2187.3		2187.2
	820.8(84)		815.9(83)	819.5(82)		814.6(81)	822.8		817.8
	$525.2(168 \times 2)$		$525.1(168 \times 2)$	$520.4(165 \times 2)$		$520.3(165 \times 2)$	511.8		511.6
DBeCl	1669.3(141)		1669.1(141)	1665.4(140)		1665.2(140)	1652.7		1652.6
	777.5(65)		772.5(64)	776.0(62)		771.0(62)	778.8		773.8
	$417.3(109 \times 2)$		$417.1(108 \times 2)$	$413.4(107 \times 2)$		$413.2(107 \times 2)$	406.2		406.0
BeCl ⁺	1014.7(201)		1009.1(202)	1009.5(200)		1003.9(200)	1007.0		1001.4
FBeCl	1399.8(403)		1399.2(402)	1411.5(383)		1410.8(382)	1419.9		1419.2
	521.2(5)		515.2(5)	520.7(6)		514.7(5)	524.3		518.2
	$291.3(89 \times 2)$		$291.0(89 \times 2)$	$289.4(87 \times 2)$		$289.1(87 \times 2)$	284.8		284.5
BeF_2		1565.0(381)			1576.5(355)			1584.2	
		725.1(0)			726.3(0)			726.9	
		$330.6(156 \times 2)$			$339.0(150 \times 2)$			333.4	
BeF		1249.1(118)			1257.0(111)			1260.5	
BeF^+		1457.7(255)			1452.6(252)			1445.8	



Figure 8. Infrared spectra in the product absorption regions for laser-ablated Be atoms and cations codeposited with SiCl₄ or CCl₄ in excess argon at 4 K: (a) Be + 0.1% SiCl₄ in Ar codeposited for 60 min, (b) after annealing to 25 K, (c) after photolysis with $\lambda > 220$ nm for 10 min, (d) after annealing to 35 K; (e) Be + 0.1% CCl₄ in Ar codeposited for 60 min, (f) after annealing to 25 K, (g) after photolysis with $\lambda > 220$ nm for 10 min, (h) after annealing to 35 K.

the 828.9 cm⁻¹ fundamental frequency for BeCl in the gas phase⁹ and to the computed values for BeCl in Table 3. In the SiCl₄ experiment HCl was observed at 2899.8 cm⁻¹ and BeH at 1986.9 cm⁻¹ (not shown); a doublet of bands at 811.8 and 806.8 cm⁻¹ is labeled HBeCl, and the case for its identification will be made as further observations are considered. We believe that HCl arises from reaction of SiCl₄ with trace water impurity during sample preparation: HCl is not observed with CCl₄. A feature at 1001.7 cm⁻¹ is marked BeCl⁺. The chlorocarbon intermediates in the top spectra using CCl₄ have been identified in previous work starting with CCl₃ radical and cation.³⁹

Figure 8 presents the analogous results using argon as the matrix host. The major triplet product starts at 1111.5 cm⁻¹, and the components are within 0.1 cm⁻¹ of the values in Figure 6. The doublets for BeCl and HBeCl are well-resolved and indicative of a single Cl atom vibration (Table 2). The band marked BeCl⁺ shifts to 995.9 cm⁻¹ in solid argon. Two additional bands are observed in the SiCl₄ experiment labeled HBeCl, one in the Be–H stretching region at 2117.6 cm⁻¹ below BeH₂ at 2159.1 cm⁻¹ first produced from the Be plus H₂ reaction⁴⁰ and one lower in the region for HBeCl bending. In addition H³⁵Cl, H³⁷Cl was observed at 2887.7, 2885.5 cm⁻¹

(not shown). To verify that HBeCl is formed through the reaction with HCl from the hydrolysis of SiCl₄ during sample preparation, the vacuum manifold was passivated with D₂O overnight, and new SiCl₄ samples were prepared and evacuated until a clean spectrum containing DCl at 2079.1, 2076.3 cm⁻¹ could be formed from the hydrolysis of SiCl₄ with D₂O. A spectrum showing new chlorine isotopic absorptions for DBeCl at 768.6 and 763.7 cm⁻¹ is compared in Figure 9 with expanded



Figure 9. Infrared spectra in the product absorption regions for laserablated Be atoms and cations codeposited with SiCl₄ or SiCl₄/D₂O in excess argon at 4 K: (a) Be + 0.5% SiCl₄/D₂O in Ar codeposited for 60 min, (b) after annealing to 25 K, (c) after photolysis with $\lambda > 220$ nm for 10 min; (d) Be + 0.1% SiCl₄ in Ar codeposited for 60 min, (e) after annealing to 25 K, (f) after photolysis with $\lambda > 220$ nm for 10 min.

absorbance scale spectra from Figure 8. Weaker HBe³⁵Cl and HBe³⁷Cl bands are still observed in the spectrum using D_2O at 800.4 and 795.6 cm⁻¹ without any intermediate bands, which confirms the presence of a single H or D atom in this product molecule. The HBeCl and DBeCl bands increase slightly on annealing and irradiation. Notice that the BeCl doublet is not shifted using D_2O to make the sample.

The CCl₄ experiment also reveals a number of chlorocarbon intermediates produced by ablation plume photolysis of CCl₄ again featuring CCl₃ radical and cation and CCl₃–Cl.^{41–45} These absorptions have been observed using different metal ablations with CCl₄ in the sample, which illustrates the role of laser plume photolysis on the matrix samples.^{20,45}

Figure 10 shows the spectra in krypton matrixes, and Table 2 lists the observed frequencies. The strong BeCl₂ triplet is observed beginning at 1102.5 cm⁻¹ and is in excellent agreement with the peaks in Figure 6. Three bands were again observed for HBeCl in the SiCl₄ experiment along with HCl at 2873.2, 2970.3 cm⁻¹ (not shown), and the SiCl₃ radical is observed at 580 cm^{-1.35}

Figure 11 illustrates infrared spectra in xenon matrixes using the Be reaction with the CCl_4 and $SiCl_4$ reagents. The $BeCl_2$ peak at 1096.1 cm⁻¹ is broader, and the isotopic components are not resolved. However, the BeCl absorption is a resolved doublet at 811.5, 806.3 cm⁻¹, but a site splitting may contribute to the lower peak as its intensity exceeds that for a single Cl atom vibration with natural abundance isotopes. The $SiCl_4$ experiment reveals weaker HBeCl bands and a weaker HCl band at 2858.6 cm⁻¹ than with the lighter matrixes. Finally, Figure S3 compares the Be reactions with $SiCl_4$ in the four noble gas matrixes.

Finally the optimized structures for product molecules based on B3LYP/6-311++g(3df,3pd)/sdd, B3LYP/cc-pVTZ, and CCSD(T)/cc-pVTZ level calculations are illustrated in Figure 12.



Figure 10. Infrared spectra in the product absorption regions for laser-ablated Be atoms and cations codeposited with SiCl₄ or CCl₄ in excess krypton at 4 K: (a) Be + 0.1% SiCl₄ in Kr codeposited for 60 min, (b) after annealing to 25 K, (c) after photolysis with $\lambda > 220$ nm for 10 min, (d) after annealing to 35 K; (e) Be + 0.1% CCl₄ in Kr codeposited for 60 min, (f) after annealing to 25 K, (g) after photolysis with $\lambda > 220$ nm for 10 min, (h) after annealing to 35 K.



Figure 11. Infrared spectra in the product absorption regions for laser-ablated Be atoms and cations codeposited with SiCl₄ or CCl₄ in excess xenon at 4 K: (a) Be + 0.1% SiCl₄ in Xe codeposited for 40 min, (b) after annealing to 25 K, (c) after photolysis with $\lambda > 220$ nm for 10 min, (d) after annealing to 35 K; (e) Be + 0.01% CCl₄ in Xe codeposited for 40 min, (f) after annealing to 25 K, (g) after photolysis with $\lambda > 220$ nm for 10 min, (h) after annealing to 35 K.

Assignments for Beryllium Dihalides. The agreement of our strong BeF₂ absorptions from Be atom reactions with F₂, ClF, CF₂Cl₂, and NF₃ in solid Ne, Ar, and Kr within 2 cm⁻¹ of measurements made for the solid BeF₂ evaporation product trapped in these matrixes¹² substantiates our assignments. This identification of BeF₂ is confirmed by B3LYP and CCSD(T) calculated frequencies (Table 3), which are 1.2, 1.9, and 2.5% higher than the observed value in solid Ne, respectively; the B3LYP value is 2.3% higher than the solid Ar observation and 2.6% higher than the solid Kr measurement, which are excellent for these levels of theory.^{20,28,29} Some of this discrepancy is due to anharmonicity in the observed frequencies not accounted for in the harmonic calculations.

The highest band at 1529.4 cm⁻¹ in solid argon is close to the 1528 cm⁻¹ assignment of Snelson to BeF₂, and the weak band in Figure 3 at 1246 cm⁻¹, which also increased on photolysis, is in agreement with that reported later by Snelson for $(BeF_2)_2$.^{12,36} Our calculations for the singlet rhombic ring structure suggested by Snelson et al.³³ find the strongest band at 1273 cm⁻¹ with 824 km/mol intensity, which substantiates these assignments.

The krypton matrix presents a new absorption at 1525.8 cm⁻¹ for BeF₂ along with a higher band at 1541.5 cm⁻¹ also observed by Snelson.¹² This higher band is probably due to an unusual matrix site like a BeF₂ molecule on the surface of a microcrystal. Recall that krypton has a much higher freezing point than argon and neon, and Kr will freeze more quickly and not as well annealed as the lighter noble gases even though we condensed our Kr samples at 17 \pm 1 K.

The three matrix values for the antisymmetric F-Be-F stretching mode are all *above* the 1520 cm⁻¹ gas-phase measurement,¹³ which is not the typical behavior for matrix-isolated molecules.³⁸ However, this relationship has been reported for noble gas complexes of BeO in matrices,² and our recent observation of BeO in neon at 1538.7 cm⁻¹ (unpublished results) has been attributed to induced-dipole

interactions involving the Ng-BeO complexes.^{2,11} Clearly the large charge on the Be center is paramount for these iondipole interactions. The Mulliken charges on BeO and its Ng complexes are given in Table S2. These charges from B3LYP/ cc-pVTZ are **0.31** for BeO itself and **0.20**, **0.12**, **0.09**, and **-0.02** for the Ng complexes. The intermatrix shifts in the frequencies (Ne-Ar, Ar-Kr, Kr-Xe) are 12.6, 4.3, and 5.1 cm⁻¹, respectively, where the largest difference between matrices is for Ne and Ar. We now make the same comparisons with the Be halides.

The linear FBeF molecule has the largest positive Mulliken charge (q) of any of our neutral molecules (Table 4). We presume that the CCSD(T) charges are more accurate than the DFT values, so we are looking at a q(Be) value of 0.706 on the Be, which is supported by two fluorides of -0.353 charge. This large charge at the Be center can sustain charge-induced dipole interactions with a number of matrix atoms, and this provides a reasonable rationale for the above series of blue matrix shifts for this linear molecule. The BeF_2 molecule has 17.1 and 3.6 cm⁻¹ shifts between Ne to Ar and Ar to Kr, and we find that the Ne-Ar separation is largest for all of the product molecules in Tables 1 and 2, and this difference is most pronounced for the BeF stretching modes of BeF₂ and BeClF (16.3 and 4.3 cm⁻¹), which has the second-largest q(Be). The large Ne-to-Ar shift can be attributed to the largest relative change in polarizability for the matrix atoms (Ne, 2.67; Ar, 11.1; Kr, 16.7; Xe, 27.3 in atomic units),⁴⁶ where the atomic polarizability increases by a factor of 11.1/2.67 = 4.2 from Ne to Ar and only 16.7/11.1 = 1.5 for Ar relative to Kr.

In the case of BeCl₂ we have agreement within 2 cm⁻¹ for measurements made for the product molecule from Be reactions with Cl₂, ClF, CF₂Cl₂, CCl₄, and SiCl₄, and within 4 cm⁻¹ of values from the evaporation of solid BeCl₂.¹² In addition we have resolution of natural abundance chlorine isotopic triplets with ~9/6/1 relative intensities (Figure 6) for a molecule with two equivalent Cl atoms. The stepwise decreases

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Figure 12. Optimized structures for product molecules based on B3LYP/6-311++g(3df,3pd)/sdd, B3LYP/cc-pVTZ (*italic*), and CCSD(T)/cc-pVTZ level (**bold**). Bond lengths are in angstroms, and bond angles are in degrees.

Table 4. Calculated Mulliken Charges for BeF, BeF₂, BeCl, BeCl₂, FBeCl, and HBeCl^a

	q(Be)	q(F)		q(F)	q(Be)	q(Cl)
BeF	0.323	-0.323	FBeCl	-0.497	0.887	-0.390
	0.231	-0.231		-0.252	0.341	-0.089
	0.349	-0.349		-0.372	0.498	-0.125
BeF_2	1.020	-0.510				
	0.492	-0.246				
	0.706	-0.353				
	q(Be)	q(Cl)		q(H)	q(Be)	q(Cl)
BeCl	0.361	-0.361	HBeCl	-0.147	0.528	-0.381
	0.071	-0.071		-0.058	0.140	-0.082
	0.126	-0.126		-0.113	0.246	-0.133
$BeCl_2$	0.822	-0.411				
	0.238	-0.119				
	0.350	-0.175				

^aCalculated with B3LYP/6-311++G(3df,3pd) level, B3LYP/cc-pVTZ level (*italic*), and CCSD(T)/cc-pVTZ level (**bold**).

in the strong antisymmetric stretching mode for $BeCl_2$ in solid Ne, Ar, Kr, and Xe (13.6, 8.9, and 6.4 cm⁻¹) are less than the first and more than the second intermatrix shifts for BeF_2 , but the total Ne-to-Kr shift for $BeCl_2$, 22.5 cm⁻¹, is slightly larger than this value for BeF_2 , 20.7 cm⁻¹, in spite of the much smaller q(Be) for $BeCl_2$, which is half of that calculated for BeF_2 . We find that only the neon matrix fundamental, 1125.2 cm⁻¹, is above the gas-phase frequency, 1113 cm⁻¹.¹³ The B3LYP frequencies for $BeCl_2$ are only 8 and 9 cm⁻¹ higher (0.7and 0.8%), the CCSD(T) frequency is 19 cm⁻¹ (1.8%) higher than the neon matrix values, and the calculated and observed chlorine isotopic splittings are the same (1.7 cm⁻¹) within 0.1 cm⁻¹.

Our Be reactions with ClF and with Cl_2/F_2 mixtures enabled the formation of BeClF through the two different reaction pathways given above. On first thought the "antisymmetric" Cl-Be-F stretching mode might fall close to the averages of these two modes for BeF₂ and BeCl₂, which are 1336 cm⁻¹ for neon and 1321 cm⁻¹ for argon and somewhat lower than the observed values of 1391.9 and 1375.6 cm⁻¹ in these two matrixes. However, the B3LYP calculated frequency for BeClF

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is 1399.8 cm⁻¹, only 8 cm⁻¹ higher than the neon matrix value with only a 0.6 cm⁻¹ separation for the chlorine 35 and 37 isotopes. This frequency is a mostly Be-F stretching mode with the largest computed intensity (403 km/mol) for any of our major products. The more symmetric Be-Cl counterpart computed at 521.5 cm⁻¹ with a 6.0 cm⁻¹chlorine isotopic shift has a very low intensity (5 km/mol) and is a mostly Be-Cl stretching mode. The intermatrix Ne-Ar and Ar-Kr shifts $(16.3 \text{ and } 4.3 \text{ cm}^{-1})$ for BeClF are nearly the same as found for BeF_{2} , although the q(Be) is slightly lower than the average of the q(Be) for the difluoride and dichloride. Agreement with the computed values for this strong Be-F stretching mode for BeClF confirms the identification of this new molecule. The small splitting of 1.4 cm^{-1} on the 1391.9 cm^{-1} band is a matrix splitting, since it is too much for the separation of chlorine isotopes.

Finally, a similar experiment was performed with Be and CF_2Cl_2 in argon, and the infrared spectra are illustrated in Figure S2. Remembering that C–Cl bonds are weaker than C–F bonds, we find the BeCl₂ absorption at 1111.5 cm⁻¹ to be considerably stronger than the BeF₂ band at 1529.1 cm⁻¹, but the sharp BeClF band at 1375.5 cm⁻¹ in this experiment was stronger than both of the former. And the 1206.6 cm⁻¹ CF₂Cl band was stronger than the 918.3 cm⁻¹ shoulder absorption for CFCl₂, where these radicals were likely produced by laser ablation plume photolysis.^{20,35} Both BeF and BeCl were observed and decreased on photolysis as will be described below. These frequencies are gathered in Table S3.

Assignments for Beryllium Hydrogen Chloride. First, examine the sharp 3/1 relative intensity doublet at 800.4 and 795.6 cm^{-1} in the argon matrix containing SiCl₄, which increases 10% upon annealing to 25 K, another 10% on broadband irradiation, and decreases 20% in final annealing to 35 K (Figures 8 and 9). Two other bands at 2117.6 and 515.6 cm⁻¹ exhibit the same behavior, and they are associated with the same new molecule, which contains a single Cl atom based on the sharp resolved 3/1 doublet just below the BeCl doublet at 817.7, 813.4 cm⁻¹. The strong band at 2117.6 cm⁻¹ falls just below BeH₂ in the Be-H stretching region,⁴⁰ so we have a new molecule containing Be-H and Be-Cl bonds. The D₂O doped experiment revealed a counterpart for DBeCl at 1613.1 cm⁻¹, and this HBeCl/DBeCl ratio 1.313 is near the calculated mode ratio 1.324 for these two product molecules and the 1.333 ratio observed for BeH/BeD.⁴⁰ Both B3LYP calculations predict the three strong IR absorptions for HBeCl (Table 3) slightly higher than the three argon matrix bands, and the CCSD(T) does so for the two higher modes, but the lowest mode is 3.8 cm⁻¹ lower. Furthermore, the calculations predict 4.9 and 5.0 cm⁻¹ chlorine isotopic components compared with the observed 4.8 cm⁻¹ value in solid argon. This frequency agreement is excellent, and it confirms the identification of HBeCl. The doublet at 800.4, 795.6 cm⁻¹ shifts to 768.6, 763.7 cm⁻¹ when D₂O was introduced into the sample manifold, as shown in Figure 9, and DCl was formed from the hydrolysis of SiCl₄. This shift also confirms that H/D is involved with these chlorine isotopic doublets having 4.8 and 4.9 cm⁻¹ splittings, and our calculations predicted 5.0 cm⁻¹. The similar HBeNC molecule has three strong modes at 2153.2, 912.4, and 525.4 cm⁻¹, and the highest (Be-H stretch)⁷ and lowest (H-Be-Cl or H-Be-N bending) modes are comparable. Finally, the first intermatrix shift for HBeCl, 11.4 cm⁻¹, is smaller than those described above for the beryllium dihalides. Our B3LYP calculations predicted these chlorine isotopic bands for DBeCl

to be at 777.5 and 772.5 cm⁻¹, which is in excellent agreement with the observed values, and confirms the identification of HBeCl and DBeCl. Similar behavior was found for these bands shifted 4–6 cm⁻¹ in a krypton matrix. This Be insertion reaction is exothermic by 85 kcal/mol.

 $Be + HCl \rightarrow HBeCl$ (6)

Assignments for Diatomic Beryllium Fluoride and Chloride. The 1242.2 cm⁻¹ (1241.6 matrix site) band in neon and its argon (1234.8 cm⁻¹) and krypton (1229.7 cm⁻¹) matrix counterparts decreased on UV photolysis, while the strong BeF_2 absorption increases. They were formed using both the F_2 and NF₃ reactions with Be, and almost the same feature, 1233.1 cm^{-1} , was observed from CF_2Cl_2 without OCF_2 nearby (Table S3). The former bands range from 13.1 to 5.7 to 0.6 cm^{-1} higher, respectively, than the gas-phase frequency (1229.1 cm⁻¹) for BeF.⁹ Our calculations predict slightly higher frequencies as expected. The B3LYP functional gives 1249.8 and 1257.0 cm⁻¹ with two different basis sets, and the CCSD(T) method obtains 1260.5 cm⁻¹, which are quite reasonable agreements with experiment for harmonic frequency calculations. Although we were not able to compute binding for a single Ng atom to BeF like we did for the cation below, the q(Be) computed (Table 4) for BeF, 0.349, is sufficient to support a stronger than typical interaction with the surrounding matrix atoms to explain the blue matrix shifts above for Ne, Ar, and Kr. BeCl has a much lower q(Be), 0.126, and the matrix shifts are all to the red of the gas phase, which is the expected relationship.

The BeCl chlorine isotopic doublets in Table 2 clearly demonstrate in the argon matrix spectra in Figures 8 and 9 that one chlorine atom is involved in this vibration, and the measured isotopic separation of 4.3 cm⁻¹ agrees with the computed values as do the frequencies themselves (compare Tables 2 and 3). The neon matrix value is 3.9 cm⁻¹ below the gas-phase value (836.7 cm⁻¹),⁹ and the heavier matrix values fall steadily lower than the neon matrix observation. This is the expected behavior for a matrix-isolated molecule.³⁸ The splitting in xenon involves a matrix site as well as Be³⁷Cl.

Assignments and Bonding for Beryllium Fluoride and Chloride Cation Complexes. The matrix spectra for the SiCl₄ reaction with Be and the Ne and Ar matrix spectra for CCl₄ reveal bands labeled NeBeCl⁺ and ArBeCl⁺. These bands share the common behavior of slightly increasing on annealing and decreasing slightly on photolysis. A 996.4 cm⁻¹ band with a 994.8 cm⁻¹ shoulder in the argon matrix from the Be and Cl₂ reaction behaves the same way as does the neon matrix counterpart at 1001.4 cm⁻¹. The broader absorption at 1445.0 cm⁻¹ in solid argon, which increases slightly on photolysis and sample annealing, and our DFT calculations revealed a very strong band at 1457.7 cm⁻¹ for the Be-F stretching mode of BeF⁺ and of Ar-BeF⁺ with the latter 50% stronger. It is interesting to note that an experiment with 1.3% each of Kr and F_2 in argon gave the same BeF_2 peak as pure argon, but the BeF⁺ peak was shifted to 1444.7, and the BeF peak shifted to 1234.1 cm⁻¹. This suggests that FBeF is not as sensitive to the noble gas environment as BeF and BeF⁺, and it follows that the Be centers in these diatomics have more room for interaction with the noble gas matrix than does FBeF. The cation peaks are labeled NgBeF⁺ or NgBeCl⁺ in the figures, because we believe that one noble gas atom binds strongly with BeF⁺ and BeCl⁺. The calculated ionization energies for these diatomic molecules are 235.4 and 230.1 kcal/mol and 225.8 and 222.5 kcal/mol

Table 5. Calculated Vibrational Frequencies (cm⁻¹), Bond Lengths, Dipole Moments, Mulliken Charges, and Binding Energies for BeF⁺ and NgBeF⁺ (Ng = Ne, Ar, Kr, Xe)^{*a*}

⁻¹) R(Ng–Be, Å) 1.676	dipole moment (D) 7.62 7.60 8.20 3.36	q(Ng)	q(Be) 1.07 1.06 1.19	q(F) -0.07 -0.06	$D_{\rm o} \ ({\rm Ng-BeF^+}, \ {\rm kcal\cdot mol^{-1}})$
1.676	7.62 7.60 8.20 3.36		1.07 1.06 1.19	-0.07 -0.06	
1.676	7.60 8.20 3.36		1.06 1.19	-0.06	
1.676	8.20 3.36		1.19	_0.10	
1.676 1.674	3.36			-0.19	
1 674		0.02	1.15	-0.12	12.1
1.0/+	3.30	0.22	0.86	-0.07	
1.672	4.66	0.17	1.03	-0.20	
1.970	2.63	0.31	0.90	-0.21	29.2
1.969	2.54	0.45	0.67	-0.12	
1.968	2.90	0.42	0.83	-0.25	
2.114	0.88	0.42	0.86	-0.38	34.8
2.112	0.81	0.53	0.60	-0.13	
2.102	1.11	0.50	0.76	-0.26	
2.300	0.36	0.60	0.61	-0.21	41.4
2.298	0.28	0.60	0.55	-0.15	
2.282	0.56	0.60	0.67	-0.27	
	1.970 1.969 1.968 2.114 2.112 2.102 2.300 2.298 2.282 (3df 3pd)/sdd level at	1.970 2.63 1.969 2.54 1.968 2.90 2.114 0.88 2.112 0.81 2.102 1.11 2.300 0.36 2.298 0.28 2.282 0.56	1.970 2.63 0.31 1.969 2.54 0.45 1.968 2.90 0.42 2.114 0.88 0.42 2.112 0.81 0.53 2.102 1.11 0.50 2.300 0.36 0.60 2.298 0.28 0.60 2.282 0.56 0.60	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

Table 6. Calculated Vibrational Frequencies (cm^{-1}) , Bond Lengths, Dipole Moments, Mulliken Charges, and Binding Energies for BeCl⁺ and NgBeCl⁺ (Ng = Ne, Ar, Kr, Xe)^{*a*}

				Ν	Aulliken chai	ge	
	frequency(Be-Cl, cm ⁻¹)	R(Ng-Be, Å)	dipole moment (D)	q(Ng)	q(Be)	q(Cl)	D₀ (Ng−BeCl⁺, kcal·mol ⁻¹)
BeCl ⁺	1014.7(201)		8.02		1.05	-0.05	
	1009.5(200)		8.07		1.25	-0.25	
	1007.0		8.83		0.72	0.27	
NeBeCl ⁺	1075.8(296)	1.683	4.56	0.03	1.01	-0.04	11.3
	1075.9(297)	1.674	4.60	0.20	0.50	0.29	
	1080.1	1.671	5.13	0.16	0.61	0.23	
ArBeCl ⁺	1078.5(363)	1.972	3.90	0.28	0.85	-0.14	26.9
	1076.7(366)	1.974	3.91	0.41	0.38	0.21	
	1087.2	1.972	4.39	0.39	0.46	0.14	
KrBeCl ⁺	1065.8(377)	2.119	1.63	0.42	0.74	-0.16	32.1
	1062.9(380)	2.118	1.67	0.50	0.32	0.18	
	1080.3	2.106	2.02	0.48	0.42	0.10	
XeBeCl ⁺	1055.3(390)	2.305	0.78	0.55	0.62	-0.17	38.0
	1051.3(389)	2.303	0.83	0.59	0.25	0.15	
	1066.6	2.293	1.27	0.58	0.32	0.09	
$a_{C} = 1 + 1$: 1 DOL VD / COLL	1)/111 1 102		1.) 1.0		1 7777 1	1 (1 11)

^aCalculated with B3LYP/6-311++G(3df,3pd)/sdd level, B3LYP/cc-pVTZ level (*italic*), and CCSD(T)/cc-pVTZ level (**bold**).

using B3LYP and CCSD(T), respectively, and the Ng atoms used here have higher first ionization energies, from Ne to Xe, namely, 497, 363, 323, and 280 kcal/mol, respectively, which are more than our computed values for BeF and BeCl. Clearly some positive charge will transfer to the Ng atoms. Our computed Mulliken charges, dipole moments, and Be-X stretching frequencies are listed in Tables 5 and 6. As we proceed down the noble gas family the lower Ng ionization energies sustain more positive charge on the Ng atom, the dipole moments decrease, and the Xe and Be charges become more nearly equal, which indicates the decrease of ionic character between Ng and Be. This change follows a decrease in the positive q(Be), while positive q(Ng) increases. For the purpose of understanding the interaction of Ng and Be, an effective method, the noncovalent interaction index (NCI) based on the relationship between the electron density $\rho(r)$ and the reduced density gradients has been introduced to study such weak long-range interation.³⁵ As depicted in Figure S4, a spike corresponding to Ne–Be located at $-(\lambda_2)\rho$ (~0.045,

lower than 0.050) in the plot of NeBeF⁺ shows stronger noncovalent interaction, while larger value of $-(\lambda_2)\rho$ (~0.057, a little higher than 0.050) in the plot of NgBeF⁺ (Ng = Ar, Kr, Xe) (Xe, not shown) suggests a weak covalent interaction.

As described in the introduction based on the Beauchamp investigations^{14,15} (and others) laser ablation generates positive metal ions and electrons,¹⁶ and we believe that vacuum UV radiation in the ablation plume is capable of photoionization of some metal atoms. Therefore, if Be⁺ reactions form molecular cations with strong infrared intensities then these positive ions can be observed in the matrix infrared spectrum. Note that the infrared intensity for BeF⁺ increases in the Ng-BeF⁺ species as Ng moves from Ne to Xe (Table 5). So the first three reactions with Be⁺ occur directly on deposition. Charge balance is assured by the ready formation of F⁻ and Cl⁻ in these experiments. The F₃⁻ anion, which could not be observed here because of instrument low-frequency limitation, is commonly observed in fluorine experiments with laser-ablated metals.⁴⁷ However, we do observe a weak band at 1378 cm⁻¹ in solid

argon, which is probably due to HF_2^- (not shown).³⁵ In addition, the stable HCl_2^- anion was formed through the reaction of HCl with Cl^- , and its two characteristic absorptions were observed at 696 and 956 cm⁻¹ in solid argon. These bands were much stronger in the SiCl₄ than in the CCl₄ experiments (Figure 8). Note that the HCl_2^- band increases on annealing and photolysis in the latter experiments. Only the stronger 738 cm⁻¹ band was observed in solid neon.^{35,48,49} Reaction 7 is exothermic by 25 kcal/mol (B3LYP/6-311++g(3df,3pd)).

$$\mathrm{HCl} + \mathrm{Cl}^{-} \to \mathrm{HCl}_{2}^{-} \tag{7}$$

In the search for new molecules that might be produced in these experiments, we found that BeF_3^- and $BeCl_3^-$ are stable to halide ion elimination by 87 and 56 kcal/mol, respectively, with strong stretching absorptions computed at 1049.6 cm⁻¹ (346 × 2 km/mol) and 718.7, 715.9 cm⁻¹ (316, 313 km/mol). The weak band at 705.6 cm⁻¹ in solid argon is tentatively assigned to $BeCl_3^-$. We did not detect HF_2^- , but a weak band (0.0023 au) in neon experiments at 1061.4 cm⁻¹ (not shown) decreases 10% on UV photolysis and increases 20% on annealing to 10 K, which can be assigned tentatively to BeF_3^- in these experiments.

$$Be^{+} + X_{2} \rightarrow [BeX_{2}^{+}]^{*} \rightarrow BeX^{+} + X$$
(8)

$$Be^{+} + X \to [BeX^{+}]^{*} \to BeX^{+}$$
(9)

$$Ng + BeX^+ \to Ng - BeX^+$$
(10)

$$Be^{+} + X_{2} \rightarrow [BeX_{2}^{+}]^{*} \rightarrow BeX_{2}^{+}$$
(11)

$$\operatorname{BeX}_2 + X^- \to \operatorname{BeX}_3^- \tag{12}$$

For X = F, the reaction energies are negative 104 and 138 kcal/ mol for 8 and 9; with Ng = Ne reaction 10 is 12 kcal/mol exothermic using CCSD(T), and Ar, Kr, and Xe = Ng follow with more exothermicity 29, 35, and 41 kcal/mol, respectively. It is interesting to note that the Ng-BeCl⁺ complexes are less bound than the fluorine analogues by 1-3 kcal/mol (Tables 5 and 6).

CONCLUSIONS

Laser-ablated Be atoms and cations react with F₂, ClF, Cl₂, NF₃, CCl₄, SiCl₄, CF₂Cl₂, HCl, and DCl diluted in noble gases upon condensation at 4 K. The major products were the dihalides BeF₂ and BeCl₂, whose identities were supported by comparison with previous evaporative work, and the new molecules BeClF and HBeCl, all of which were confirmed by vibrational frequency calculations at the B3LYP and CCSD(T)levels of theory. The matrix-isolated BeF molecule fundamental frequency is higher, and the BeCl frequency is lower, than deduced for the gas-phase molecules, respectively. The BeF⁺ and BeCl⁺ cations formed strong dipole-induced dipole complexes in solid Ne, Ar, Kr, and Xe with stepwise increase in computed noble gas dissociation energies, respectively. Going down the family Ng-BeF⁺ and Ng-BeCl⁺ (Ng = Ne, Ar, Kr, Xe) series the Mulliken charges q(Be) decrease, while q(Ng) increase and the dipole moments decrease, which suggests increased covalent bonding in the xenon species. The hydride chloride HBeCl was observed in the SiCl₄ experiments owing to partial hydrolysis of SiCl₄ to HCl during sample preparation, which was confirmed by treating the manifold with D₂O, and absorptions for DCl and DBeCl appeared in the spectra. Laser-ablated electrons lead to the formation of Cl-,

which reacts with HCl to form the stable HCl_2^- anion. Finally, BeX_3^- anions are also stable, and tentative identifications of BeF_3^- and $BeCl_3^-$ are proposed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b09454.

Calculated vibrational frequencies, intensities, and Cartesian coordinates of the observed products. Infrared spectra using CIF and CF₂Cl₂ precursors (PDF)

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Notes

The authors declare no competing financial interest.

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